$-\Delta H_1$ (dimethylamine) $= 12{,}470 + 0.35149N$ and $-\Delta H_2$ (trimethylamine) $= 12{,}344 + 0.31645N$. The experimental values agree with the values calculated by these relations on the average to 0.43%; the maximum deviation is 0.93%.

AUSTIN, TEXAS

RECEIVED JULY 25, 1938

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

# The Densities of Fine Powders. II

BY J. L. CULBERTSON AND MARTIN K. WEBER

In a recent study of the apparent densities of fine powders made in this Laboratory[1] the differences in values obtained when different liquids were used as the buoying fluids were noted and conclusions were reached which were somewhat at variance, in their detail, from those reached by previous investigators. In a second study[2] there was evident a rough correlation between apparent density values and the heats of wetting of the powders when wetted by the same liquids. Further studies seemed desirable in order to test the conclusions reached in that work, and it was proposed that these should be developed along two lines, namely, (a) density determinations should be made of the fine powders used in the previous work (silica gel and active, practically ash-free, charcoal) using a number of liquids not yet investigated and (b) a study should be made of apparent densities of a non-porous powder in liquids of different types.

In the previous work[1] the conclusion was reached that variations in the apparent density of a porous powder might be due either to differences in the degree of penetration of the porous solid by the liquids or to differences in the degree of compression of the liquids at the solid–liquid interface. In either case the density differences noted must have been due primarily to the differences in surface energy decrease on wetting the solid, though in the second case differences in the compressibilities of the liquids would have been a conditioning factor. The measurements on a non-porous powder were proposed with the hope that by such means the first of these possible explanations might be confirmed or disproved.

**Experimental.**—In the previous work[1] a modification of the method of Harkins and Ewing[3] was used. Since this method requires considerable time, the method used by Tschapek[4] was investigated. This in brief consists of weighing a sample of the solid into a suitable specific gravity bottle and adding to the sample liquid sufficient to submerge it. The bottle is then placed in a vessel provided with suitable means of air-tight closure and a connection to a vacuum pump. This vessel is then evacuated to a pressure slightly below the vapor pressure of the liquid used on the sample. With such a pressure the adsorbed air is removed rapidly from the surface of the solid particles and after a sufficient time period (determined by increasing to time intervals yielding constant value determinations) the vacuum is broken, the specific gravity bottle filled, brought to the standard temperature and weighed. After making the necessary buoyancy corrections, the density is calculated directly. Tests of this method in comparison with that used in the previous work[1] demonstrated a satisfactory agreement, and, since it is considerably faster than the one formerly used, it was adopted for the present investigations.

**Results and Discussion.**—In the first study, samples of the same solid materials as were used previously[1] were employed. These were powdered silica gel and active ash-free charcoal. The methods for their preparation have been described.[1] Water, benzene, nitrobenzene, carbon disulfide, acetone, ethyl alcohol, and *n*-butyl alcohol were purified carefully by standard methods and used in the density determinations. The density values for each of the solids in each liquid are given in Table I(a). It is of interest also to add to these values those of Table I(b) taken from the previous work.

TABLE I(a)

| Liquid used | Density values, g./cc. at 25°<br>$SiO_2$ | C |
|---|---|---|
| Acetone | 2.310 | 2.047 |
| Ethyl alcohol | 2.248 | 2.012 |
| Water | 2.247 | 1.861 |
| Nitrobenzene | 2.239 | 2.011 |
| *n*-Butyl alcohol | 2.236 | 1.976 |
| Carbon disulfide | 2.216 | 2.029 |
| Benzene | 2.183 | 2.005 |

TABLE I(b)

| | | |
|---|---|---|
| Carbon tetrachloride | 2.13 | 1.86 |
| Petroleum ether | 2.12 | 2.08 |

Harkins and Ewing found charcoal density to be a function of the compressibility of the liquid

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[1] Culbertson and Dunbar, THIS JOURNAL, **59**, 306 (1937).

[2] Culbertson and Winter, *ibid.*, **59**, 308 (1937).

[3] Harkins and Ewing, *ibid.*, **43**, 1787 (1921).

[4] M. W. Tschapek, *Kolloid-Z.*, **63**, 343 (1933).

used in the determination and in consideration of the fact that the charcoals were of different origins the data above are in satisfactory agreement with their values. As noted in the previous paper,[1] however, the observed values of the density of silica do not agree with such a concept. It appears significant that those liquids possessing the greatest compressibility yield the greatest values for the density of charcoal, while those with polar groupings, as indicated by high electric moment, show the greatest values for the density of silica; considering specific cases, the dipole moment of acetone is high and its compressibility is comparatively high. The density values of both charcoal and silica are high when determined by means of acetone. Water with high dipole moment and low compressibility yields a high density for silica and low density for charcoal, while petroleum ether with high compressibility and zero dipole moment yields a low density for silica and a high density for charcoal. The reader will of course observe that the extreme cases have been mentioned in illustrating the point made, and further that in some cases, particularly that of the density of charcoal in carbon tetrachloride and perhaps that of silica in carbon disulfide, the suggested relationship is not apparent. The data, however, offer considerable support for the generalization made. To the writers this would seem to indicate that on the silica surface polar groups are oriented to the interface and the large force of attraction causes compression of the liquid. Non-polar liquid molecules under the influence of less attractive force and feeble orienting influence even though of high compressibility fail to show such high densities for this solid. Generally speaking, opposite orientations and large forces of attraction between solid and non-polar groups and molecules seem to be indicated for the charcoal.

The data may, however, be explained on the basis of penetrability of the porous solids by the various liquids and the second series of determinations appear to be significant in this connection. For this study selected crystals of clear quartz were crushed and then ground in a pebble mill. The charge was removed from the mill at frequent intervals and screened. All material passing a 200-mesh sieve was retained and the rest returned to the mill. When approximately two pounds (1 kg.) of the 200-mesh material had been accumulated, the coarse fraction was discarded and the fine powder mixed and sampled. The fine material was then returned to the mill and the grinding continued for a period of five hundred hours, samples being taken at intervals. After approximately one hundred and twenty-five hours grinding, caking of the charge became so troublesome that the grinding was continued with the charge in the form of a slurry. The samples taken from the slurry were dried for twenty-four hours at 110°. Using the same method as was used in obtaining the data of Table I, the densities of these samples were determined using pure water and benzene. The results are given in Table II.

TABLE II

DENSITY OF GROUND QUARTZ

G./cc. at 25°

| Grinding time, hours | Determination made in Water | Benzene |
|---|---|---|
| 0 | 2.643 | |
| 4 | 2.642 | |
| 12 | 2.644 | |
| 24 | 2.641 | |
| 48 | 2.642 | 2.643 |
| 96 | 2.636 | 2.636 |
| 136 | 2.632 | 2.636 |
| 204 | 2.615 | 2.614 |
| 300 | 2.602 | 2.592 |
| 375 | 2.585 | 2.561 |
| 500 | 2.553 | 2.535 |

In the interpretation of these data cognizance must first be had of the falling trend of values as grinding is continued. This effect has been observed with ground quartz by Martin, *et al.*,[5] and the explanation has been offered that a part of the surface layer of the particles has been converted into amorphous material of lower density than the quartz crystal.[6] If this be the correct interpretation, then the relation between the two series of values becomes significant. Until well past two hundred hours of grinding, the density measurements in the two liquids show no appreciable differences, but from three hundred hours onward, the measurements in benzene fall definitely below those made in water. If it may be assumed that this material is non-porous, then only one of the suggested explanations will be applicable; *i. e.*, the water must be more strongly compressed at the interface than the benzene, the effect becoming evident only when a high

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(5) Alexander, "Colloid Chemistry," Vol. III, The Chemical Catalog Co., New York, N. Y., p. 305.

(6) That the effect cannot be due to attrition of the pebbles in the mill seems assured from the fact that the mean density of the pebbles was 2.577 g./cc. which, though much less than that of the original quartz, is appreciably greater than the final values obtained.

degree of subdivision is attained. Positive assurance can be had, however, only when the surface structure of the quartz particles is definitely known.

## Summary

Density measurements of silica and charcoal, using a series of liquids as the buoying fluid, indicate that polar liquids yield high density values for silica, non-polar yield low values. The more compressible liquids yield the higher density values for charcoal. Polar liquids having large compression coefficients yield high density values for both solids.

Density measurements of ground quartz of varying degrees of fineness were made by means of benzene and water as the buoying fluids. These measurements confirm the foregoing statements and indicate that a different degree of penetration of different liquids into the surface of the solid is probably not a factor of significance in the variations of apparent density.

PULLMAN, WASH. RECEIVED AUGUST 22, 1938

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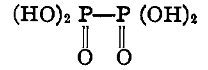
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 652]

# An Attempted Exchange of Phosphorus between Phosphorous and Phosphoric Acids

BY J. NORTON WILSON

The hydration of hypophosphoric acid, which takes place according to the equation

$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4 \qquad (1)$$

has been shown[1,2] to proceed at a rate which is first order with respect to hypophosphoric acid and increases with increasing hydrogen ion concentration. It has been suggested[1] that this reaction is irreversible, but it seems probable that an equilibrium may be reached in which the concentration of hypophosphoric acid remaining is too small to be detected readily by chemical methods. If the structure of hypophosphoric acid is such that the phosphorus atoms are equivalent, as in the structure  $(HO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{O}{\|}}{P}(OH)_2$ which has been suggested on the basis of X-ray absorption spectra and chemical properties by Nylen and Stelling[3] and by Hantzsch,[4] the reverse of reaction (1) should lead to an exchange of radioactive phosphorus between phosphorous and phosphoric acids according to the following mechanism (the radioactive phosphorus atom is denoted by an asterisk)

$$H_3P^*O_4 + H_3PO_3 \rightleftarrows H_2O_3P^* - PO_3H_2 + H_2O \rightleftarrows H_3P^*O_3 + H_3PO_4 \qquad (2)$$

An attempt has been made to detect this exchange using radioactive phosphorus[5] obtained as a by-product of the formation of radio-sulfur by bombardment of sulfur with fast deuterons. The material was separated from most of the accompanying sulfur and oxidized to phosphoric acid; a small amount of ordinary phosphoric acid was added as a carrier. The phosphate was precipitated as magnesium ammonium phosphate and converted to lead phosphate which was treated with hydrogen sulfide to liberate radioactive phosphoric acid. The reaction mixtures were made up from this material and "C. P." phosphorous and phosphoric acids. The phosphorous acid used was found to contain a small amount of phosphoric; this was determined and corrected for.

In order to determine whether exchange had occurred the mixture was diluted and the phosphate precipitated as magnesium ammonium phosphate; this was dissolved in acid and reprecipitated to remove co-precipitated phosphite. The phosphate precipitate was dried and its electroscopic activity measured. The phosphite contained in the filtrates was oxidized with bromine and similarly precipitated; the electroscopic activity of this precipitate was determined as before. Occurrence of activity in the latter precipitate would be evidence either of exchange or faulty separation.

The reaction mixtures were made up in duplicate; one of the pair, used as a blank, was subjected immediately after mixing to the separation process and radioactivity measurements described above; the other was sealed in a glass

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(1) Van Name and Huff, *Am. J. Sci.*, **45**, 103, 18 (1918).

(2) Blaser, *Z. physik. Chem.*, **A167**, 441 (1934).

(3) Nylen and Stelling, *Z. anorg. allgem. Chem.*, **212**, 169 (1933); *ibid.*, **218**, 301 (1934).

(4) Hantzsch, *ibid.*, **221**, 63 (1934).

(5) This material was supplied through the generosity of Professor Edwin McMillan of the Radiation Laboratory of the University of California.